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(54) DYE-SENSITIZED PHOTOELECTRIC CONVERSION ELEMENT

(57)Abstract:
PROBLEM TO BE SOLVED: To develop an inexpensive photoelectric conversion element using a dye expressed by the general formula (1) and having excellent conversion efficiencyand a solar battery. (In the formulaAr1 and Ar2 express an aroma ring or a heterocyclic ringeach of which may have a substitute. XYZ express an hydrogen atom or a substitute).
SOLUTION: This solar battery uses the photoelectric conversion element formed of a thin film of an organic dye sensitized semiconductor corpuscleand the thin film is made to carry the dye expressed by the general formula (1).

CLAIMS

[Claim(s)]
[Claim 1]An optoelectric transducer using an oxide semiconductor particle by which sensitization was carried out with coloring matter expressed with a general formula (1).

[Formula 1]

(Ar1 and Ar2 show among a formula the aromatic ring or heterocycle which may have a substituentrespectively.) XYand Z express a hydrogen atom or a substituentrespectively.
[Claim 2]The optoelectric transducer according to claim 1 which is an aromatic ring in which Ar1 and Ar2 may have a substituentrespectively.
[Claim 3]An optoelectric transducer given in claims 1 thru/or 2wherein Ar1 and Ar2 are the benzene rings thru/or naphthalene rings which may have a substituentrespectively.
[Claim 4]An optoelectric transducer given in claims 1 thru/or 3 having at least one or more of a carboxyl groupa hydroxyl groupa sulfonic groupa phosphate groupan amide groupand sulfhydryl groups in intramolecular.
[Claim 5]An optoelectric transducer using an oxide semiconductor by which united among compounds chosen from a group which consists of organic coloring matter which has one or more coloring matter given in claims 1 thru/or 4other metal complexesand other structures at leastand sensitization was carried out with two or more compounds.
[Claim 6]An optoelectric transducer given in claims 1 thru/or 5 in which an oxide semiconductor particle contains a titanium dioxide as an essential ingredient.
[Claim 7]An optoelectric transducer given in claims 1 thru/or 6 which made an oxide semiconductor particle support coloring matter under existence of an inclusion compound.
[Claim 8]An optoelectric transducer given in any 1 paragraph of claims 1 thru/or 7 produced by making a thin film which consists of oxide semiconductor particles support coloring matter.
[Claim 9]A solar cell using an optoelectric transducer of a statement for any 1 paragraph given in claims 1 thru/or 8.
[Claim 10]An oxide semiconductor particle by which sensitization was carried out with coloring matter expressed with a general formula (1).

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which this invention belongs] This invention relates to the optoelectric transducer and solar cell using the

semiconductor particulate by which sensitization was carried out with organic coloring matterand is a general formula (1) in detail. It is related with the solar cell using the optoelectric transducer and it using the oxide semiconductor particle by which sensitization was carried out with the coloring matter expressed.

[0002]

[Description of the Prior Art]The solar cell which uses sunlight as an energy resource replaced with fossil fuelssuch as petroleum and coalattracts attention. Nowdevelopment examinationsuch as efficient-izingis briskly made about the compound semiconductor solar cell using a crystalthe silicon solar cell using amorphous silicon or galliumarsenicetc. etc. Howeversince they have high energy and cost which manufacture takesthere is a problem that it is difficult to use it general-purpose. The optoelectric transducer using the semiconductor particulate which carried out sensitization with coloring matteror the solar cell using this is also knownand the material and production technology which create this are indicated. (B. O'Regan and M. Graetzel Nature353737 (1991)M. K. NazeeruddinA. KayI. RodicioR. Humphry-BakerE. MullerP. LiskaN. VlachopoulosM. GraetzelJ. Am. Chem. Soc. 115and 6382 (1993) e. t. c. -- this optoelectric transducer being manufactured using comparatively cheap oxide semiconductorssuch as titanium oxideandThe cheap optoelectric transducer of cost may be obtained compared with the solar cell using conventional silicon etc. and attention is attracted. Howeverin order to obtain an element with high conversion efficiencythe complex of the ruthenium series was used as sensitizing dyethe cost of coloring matter itself is highand the problem remains also in the supply. Although the trial using organic coloring matter as sensitizing dye has also already been performedit is in the actual condition of not resulting in utilization yet -- conversion efficiency is low.

[0003]

[Problem(s) to be Solved by the Invention]In the optoelectric transducer using an organic-coloring-matter sensitization semiconductordevelopment of the high optoelectric transducer of practicality with high conversion efficiency is called for using cheap organic coloring matter.

[0004]

[Means for Solving the Problem]In order to solve the above-mentioned technical problemas a result of trying hard wholeheartedlythis invention persons do sensitization of the semiconductor particulate using coloring matter expressed with the above-mentioned general formula (1)find out that an optoelectric transducer with high conversion efficiency is obtained by creating an optoelectric transducerand came to complete this

invention. Namelythis invention [0005](1) An optoelectric transducer using an oxide semiconductor particle by which sensitization was carried out with coloring matter expressed with a general formula (1)[0006]
[Formula 2]

[0007](Ar1 and Ar2 show among a formula the aromatic ring or heterocycle which may have a substituentrespectively.) XYand Z express a hydrogen atom or a substituentrespectively.
(2) The optoelectric transducer given in (1) which is an aromatic ring in which Ar1 and Ar2 may have a substituentrespectively(3) (1) thru/or the optoelectric transducer given in (2) being the benzene ring thru/or the naphthalene ring in which Ar1 and Ar2 may have a substituentrespectivelyTo intramolecular(4) A carboxyl groupa hydroxyl groupa sulfonic groupa phosphate groupan amide group(1) thru/or the optoelectric transducer given in (3) having at least one or more of sulfhydryl groups(5) The inside of the compound chosen from the group which consists of organic coloring matter which has one or more coloring matter (1) thru/or given in (4)other metal complexesand other structures at leastThe optoelectric transducer using the oxide semiconductor by which united and sensitization was carried out with two or more compounds(6) (1) thru/or the optoelectric transducer given in (5) in which an oxide semiconductor particle contains a titanium dioxide as an essential ingredient(7) An optoelectric transducer given in any 1 paragraph of (1) thru/or (7) acquired by making the thin film which consists of an optoelectric transducer (1) which made the oxide semiconductor particle support coloring matter under existence of an inclusion compound thru/or given in (6)and (8) oxide semiconductor particles support coloring matterIt is related without the oxide semiconductor particle by which sensitization was carried out with the solar cell using the optoelectric transducer of a statement for any 1 paragraph (9)(1)or given in (8)and the coloring matter expressed with (10) general formulas (1).
[0008]
[Embodiment of the Invention]This invention is explained in detail below. The optoelectric transducer of this invention uses the oxide semiconductor by which is coloring matter expressed with a general formula (1)and sensitization was carried out.
[0009]
[Formula 3]

[0010]As the substituents X and Y in a general formula (1)respectively Especiallythe aliphatic hydrocarbon group which may have a substituent although there is no restrictionThe amino group which may have a substituentthe aromatic hydrocarbon residue which may have a substituentThe heterocyclic residuethe substitutionor the unsubstituted sulfhydryl group which may have a substituentA hydrogen atoma halogen atoman alkoxy groupan alkoxycarbonyl groupSubstitution carbonyl groupssuch as a carboxyl groupa carbo amide groupand an acyl groupA sulfonic groupa sulfamoyl groupa tosyl groupa cyano groupan isocyano groupA tiocyanato groupan isotiocyanato groupa nitro groupa nitrosyl groupa hydroxyl groupThe aliphatic hydrocarbon group which a phenoxy groupa phosphate groupa phosphoester groupetc. are mentionedand may have a substituentThe amino group which may have a substituentthe aromatic hydrocarbon residue which may have a substituentthe heterocyclic residue which may have a substituenta carboxyl groupa hydroxyl groupa sulfonic groupa phosphate groupa sulfhydryl groupetc. are preferredand a carboxyl groupa hydroxyl groupa sulfonic groupand a phosphate group are still more preferred. The aliphatic hydrocarbon group which may express the heterocyclic residue which may have the aromatic hydrocarbon residue or the substituent which may have a hydrogen atoman aliphatic hydrocarbon group which may have a substituentand a substituent as the substituent Zand may have a hydrogen atom and a substituent is preferred.
[0011]A straight chain of saturation which may have a substituent as an aliphatic hydrocarbon groupand an unsaturationbranchingand an annular aliphatic hydrocarbon group are mentioneda carbon number is a straight chained alkyl group of saturation in which 1 to 36 may have a substituent desirable still more preferablyand that whose carbon number is 1 to 20 is mentioned. Cycloalkyl of the carbon numbers 3 thru/or 8etc. are mentioned as an annular thing. As a typical examplea methyl groupan ethyl groupn-propyl groupan iso-propyl groupn-butyl groupan iso-butyl groupa ter-butyl groupan octyl groupAn octadecyl groupan isopropyl groupa cyclohexyl groupa vinyl groupa propenyl groupiso [a pentynyl groupa butenyl groupa hexenyl groupa hexa dienyl group an isopropenyl group and] -- a xenyl group and cyclo -- a xenyl groupa cyclopentadienyl groupan ethynyl groupa propynyl groupand a pentynyl group -- it passesand a KISHINIRU group is mentioned iso [a KISHINIRU group and] and a KISHINIRU group etc. are mentioned to cyclo.
[0012]Aromatic hydrocarbon residue means a basis excluding one hydrogen atom from aromatic hydrocarbonFor examplea basis excluding one hydrogen atom from aromatic hydrocarbonsuch as

benzenenaphthaleneanthracenephenanthrenepyreneindenean azulenea fluoreneand peryleneis mentionedand as these were described aboveall may have a substituent. Usuallyit is the aromatic hydrocarbon residue which has the aromatic rings (condensed ring containing an aromatic ring and an aromatic ring) of the carbon numbers 6 thru/or 16. Heterocyclic residue means a basis excluding one hydrogen atom from a heterocyclic compound. As heterocyclic residuefor examplepyridinepyrazinepyrimidinea pyrazolePyrazolidinethiazolidineoxazolidinePirana chromenePyrrolebenzimidazoleimidazolineimidazolidineimidazoleA pyrazoletriazoletriazinediazolemorpholineIndeneindolinea thiophenea francthiazinea thiazoleIndorebenzothiazolenaphthothiazoleoxazolbenzooxazolnaphthooxazol India reninbenzo INDO reninpyrazinequinolinequinazolinecarbazoleetc. are mentioned -- each heterocyclic residue -- **** -- it may be hydrogenatedand these may have a substituent again so that it may describe above.

[0013]As a substituent in heterocyclic residue which may have aromatic hydrocarbon residue or a substituent which may have an aliphatic hydrocarbon group which may have a substituentand a substituentAlthough there is no restriction in particularan alkyl groupan aryl groupa cyano groupan isocyano groupA tiocyanato groupan isotiocyanato groupa nitro groupa nitrosyl groupan acyl groupA halogen atomhydroxyla phosphate groupa phosphoester groupsubstitutionor an unsubstituted sulfhydryl groupSubstitution carbonyl groupssuch as substitution or an unsubstituted amino groupsubstitution or an unsubstituted amide groupan alkoxyl groupan alkoxyalkyl groupan alkoxycarbonyl groupa carboxyl groupa carbo amide groupand an acyl groupa sulfonic groupetc. are mentioned. The meaning same as an alkyl group as the above-mentioned is expressedand these alkyl groups may be further replaced by the above-mentioned substituent (except for an alkyl group). A basis etc. which took a hydrogen atom as an aryl group from an aromatic ring mentioned by a paragraph of aromatic hydrocarbon residue are mentioned. An aryl group may be replaced by the further above-mentioned substituent etc. As an acyl groupan alkyl carbonyl group of the carbon numbers 1 thru/or 10an arylcarbonyl groupetc. are mentionedand an acetyl groupa propionyl groupetc. are preferably mentioned to an alkyl carbonyl group of the carbon numbers 1 thru/or 4and a concrete target. Atomssuch as chlorinebromineand iodineare mentioned as a halogen atom. As a phosphoester groupa phosphoric acid (carbon numbers 1 thru/or 4) alkyl ester group etc. are mentioned. A sulfhydryl groupan alkyl sulfhydryl groupetc. are mentioned as substitution or an unsubstituted sulfhydryl

group. An amino group and mono- **** as substitution or an unsubstituted amino group A dialkylamino groupAs for mono- ****a JI aromatic amino group etc. are mentionedas for mono- ****as for a diethylamino group and mono- ****a dipropylamino group is mentioned**** [mono-]as for a dimethylamino group and mono- ****a diphenylamino group or a benzylamino group is mentioned. It may combine with a core like a durolysine ringand heterocycle may be formed. As substitution or an unsubstituted amide groupan amide groupan alkylamide groupan aromatic amide groupetc. are mentioned. As an alkoxyl groupan alkoxyl group of the carbon numbers 1 thru/or 10etc. are mentionedfor example. As an alkoxyalkyl groupan alkoxy (carbon numbers 1 thru/or 10) alkyl group etc. are mentionedfor example (carbon numbers 1 thru/or 10). As an alkoxycarbonyl groupan alkoxycarbonyl group of the carbon numbers 1 thru/or 10etc. are mentionedfor example. Acidic groupssuch as a carboxyl groupa sulfonic groupand a phosphate grouplithiumA salt like quarternary ammonium saltsuch as metal salt and tetramethylammoniumsuch as sodiumpotassiummagnesiumand calciumtetrabutylammoniumpyridiniumand imidazoliummay be formed. Coloring matter expressed with a general formula (1) may have a counter ion. As a counter ionalthough limitation in particular is not carried outa common anion may be sufficient as it. As an exampleF $^-$ Cl $^-$ Br $^-$ I $^-$ ClO_4^- BF_4^- PF_6^- OH^- SO_4^{2-} $CH_3SO_3^-$ toluenesulfonic acidThey are mentioned by anion etc. which have COO^- and Br $^-$ I $^-$ ClO_4^- BF_4^- PF_6^- $CH_3SO_3^-$ toluenesulfonic acidAn anion etc. which have COO^- are preferred. It may be neutralized by acidic groupssuch as a carboxyl group between not a counter ion but intramolecularor a molecule. Ar1 and Ar2 in a general formula (1) show an aromatic ring or heterocyclerespectively. As an aromatic ringthe benzene ringa naphthalene ringan anthracene ringa phenanthrene ringThey are mentioned by a pyrene ringa perylene ringan indene ringan azulene ringfluorene ringetc.and as heterocycleA pyridine ringa pyrazine ringa bipyridine ringa piperidine ringa piperazine ringA morpholine ringa phenanthroline ringan indoline ringa thiophene ringa furan ringan oxazole ringa thiazole ringan indole ringa benzothiazole ringa benzo oxazole ringa pyrazine ringa quinoline ringa quinoxaline ringa carbazole ringetc. are mentioned. As Ar1 and Ar2the benzene ring and a naphthalene ring are preferred. Ar1 and Ar2 may be mutually the sameor they may differ.

[0014]Ar1 and Ar2 may have a substituentrespectively. A substituent shown here may be the same as that of a thing quoted by a paragraph of the above-mentioned substituents X and Y. When it may exist and exists [two or more]independently same respectively substituent may be sufficient as two or more substituents of Ar1 and Ar2and they may differ. Coloring matter which has the structure of a general formula (1) to intramolecular Anywayat least one or more carboxyl groupsIt is preferred for adsorption combination with an oxide semiconductor to have substitution carbonyl groupssuch as an alkoxycarbonyl groupa carvone amide groupand an acyl grouphydroxyla sulfonic groupand a phosphate group. Coloring matter expressed with a general formula (1) may form metal and complexessuch as nickelZnand Cu.

[0015]As a typical thing of coloring matter expressed with a general formula (1)kino FUTARON is mentionedfor example. This kino FUTARON an aromatic acid anhydride2-methylquinolineetc. NN-dimethyl sulfoxideIt is obtained by making it condense at 150 ** - about 200 ** using catalystssuch as zinc chloride and p-toluenesulfonic acidamong high boiling point solventssuch as N-methyl pyrrolidonechlorobenzenealt.dichlorobenzenetrichlorobenzeneand sulfolane.

[0016]

[Formula 4]

[0017]Kino FUTARON takes mutually a conjugate structural isomer shown below.

[0018]

[Formula 5]

[0019]The examples of a compound are enumerated below. Both Ar1 and Ar2 express the example of the compound which is the benzene ring to Table 1 as the following general formulas (2). NDM in front shows N and N-dimethylamino groupNDE shows N and N-diethylamino group and NDP shows N and N-diphenylamino grouprespectively.

[0020]

[Formula 6]

[0021]

[Table 1]

[0022]As an example of other coloring matter of thesethe following are mentionedfor example.

[0023]

[Formula 7]

[0024]

[Formula 8]

[0025]Ar1 expresses with the benzene ring the example of the compound whose Ar2 is a naphthalene ring to Table 2 as the following general formulas (3). NDM in front shows N and N-dimethylamino groupNDE shows N and N-diethylamino group and NDP shows N and N-diphenylamino grouprespectively.

[0026]

[Formula 9]

[0027]

[Table 2]

[0028]As an example of other coloring matter of thesethe following are mentionedfor example.

[0029]

[Formula 10]

[0030]With a naphthalene ringAr1 expresses the example of the compound whose Ar2 is the benzene ring to Table 3 as the following general formulas (4). NDM in front shows N and N-dimethylamino groupNDE shows N and N-diethylamino group and NDP shows N and N-diphenylamino grouprespectively.

[0031]

[Formula 11]

[0032]

[Table 3]

[0033]As an example of other coloring matter of thesethe following are mentionedfor example.

[0034]

[Formula 12]

[0035]Both Ar1 and Ar2 express the example of the compound which is a naphthalene ring to Table 4 as the following general formulas (5). NDM in front shows N and N-dimethylamino groupNDE shows N and N-diethylamino group and NDP shows N and N-diphenylamino grouprespectively.

[0036]

[Formula 13]

[0037]

[Table 4]

[0038]As an example of other coloring matter of thesethe following are mentionedfor example.

[0039]

[Formula 14]

[0040]The following are mentioned as an example of coloring matter other than these general formula (2) - (5).

[0041]

[Formula 15]

[0042]The dye sensitizing optoelectric transducer of this invention manufactures the thin film of an oxide semiconductor on a substrate using an oxide semiconductor particleandsubsequently to this thin filmmakes coloring matter support. Although that in which the surface is conductivity as a substrate which provides the thin film of an oxide semiconductor by this invention is preferredit is easily available in a commercial scene in such a substrate. On the surface of a polymer material with transparencysuch as the surface of glasspolyethylene terephthalateor polyether sulphonespecificallyfor example IndiumWhat provided the thin film of metalsuch as conductive metallic oxidesuch as tin oxide which doped fluoride and antimonycoppersilverand goldcan be used. As the conductivitywhat is necessary is just usually 1000ohms or lessand especially a thing of 100ohms or less is preferred. As particles of an oxide semiconductora metallic oxide is preferredand oxidessuch as titaniumtinzinctungstena zirconiumgalliumindiumyttriumniobiumtantalumand vanadiumare mentioned as the example. Oxidessuch as titaniumtinzincniobiumand tungstenare [among these] preferredand titanium oxide is [among these] the most preferred. These oxide semiconductors can also be used mixingalthough it is single and can also be used. As mean particle diameterthe particle diameter of the particles of an oxide semiconductor is usually 1-500 nmand is 5-100 nm preferably. The particles of this oxide semiconductor can also mix and use the thing of big particle diameterand the thing of small particle diameter. A way an oxide-semiconductor thin film forms an oxide semiconductor particle as a thin film on a substrate directly by spray spraying etc.After applying on a substrate the slurry of the method and semiconductor particulate as for which a substrate deposits a semiconductor particulate film electrically as an electrodeit can manufacture by dryinghardening or calcinating. The method of using a slurryetc. are preferred on the performance of an oxide semiconductor electrode. In the case of this methoda slurry is obtained by distributing the oxide semiconductor particle condensed the 2nd order so that primary [an average of] particle diameter may be set to 1-200 nm into carrier fluid with a conventional method. It is [anything] good if a semiconductor particulate may be distributed as carrier fluid which distributes a slurryIt is preferred for organic solventssuch as hydrocarbonsuch as ketonesuch as alcoholsuch as water or ethanolacetoneand an acetylacetoneor hexaneto be usedand to mix and use theseand to use water at the point of lessening viscosity change of a slurry. Not less than 300 ** of calcination temperature of the substrate which applied the slurry is usually not less than 400 ** preferablyand a maximum is below the melting point (softening temperature) of a substrate in generaland a maximum is 900 ** and is usually 600 ** or less preferably. Although there is no limitation in particular in firing timeless than 4 hours is preferred in general. The thickness of the thin film on a substrate is usually 5-50 micrometers preferably in 1-200 micrometers. Secondary treatment may be performed to an oxide-semiconductor thin film. Namelyfor examplea thin film can be made to be able to dip in solutionssuch as alkoxide of the same metal as a semiconductora chloridea nitrification thingand a sulfidethe whole substrate directlyand the performance of semiconductor membrane can also be raised desiccation or by re-calcinating. As metal alkoxidetitanium ethoxidea titanium iso PUROPOKI sidetitanium t-butoxiden-dibutyldiacetyltinetc. are mentionedand the alcohol solution is used. As a chloridetitanium tetrachloridea tin tetrachloridezinc chlorideetc. are mentionedand the solution is used.

[0043]Nexthow to make an oxide-semiconductor thin film support coloring matter is explained. If it is in a solution which

dissolved and obtained coloring matter as a method of making the aforementioned coloring matter supportingwith a solvent which may dissolve coloring matteror soluble low coloring mattera method of immersing a substrate with which the above-mentioned oxide-semiconductor thin film was provided is mentioned to dispersion liquid obtained by making distribute coloring matter. Concentration in a solution or dispersion liquid is suitably decided with coloring matter. Semiconductor membrane created on a substrate is dipped into the solution. Dipping time is from ordinary temperature to the boiling point of a solvent in generaland dipping time is about 48 hours from 1 hour. As an example of a solvent which can be used for dissolving coloring mattermethanolethanolacetonitriledimethylsulfoxidedimethylformamideetc. are mentionedfor example. As for dye density of a solution1x10-6M - 1M are usually goodand it is ix10-5M-1x10-1M preferably. Thusan optoelectric transducer of an oxide semiconductor particle thin film which carried out sensitization with coloring matter is obtained. The number of coloring matter to support may be oneand it may be mixed in some numbers. When mixingthe coloring matter of this invention may be sufficientand other coloring matter and metal complex coloring matter may be mixed. By mixing the coloring matter from which especially an absorption wavelength differsa broad absorption wavelength can be used and a solar cell with high conversion efficiency is obtained. Although there is no restriction in particular as an example of a metal complex to mix J. Am. Chem. Soc. 115a ruthenium complex and phthalocyanine that are shown in 6382 (1993) or JP2000-26487APorphyrin etc. are preferred and coloring mattersuch as methine system coloring mattersuch as phthalocyanine of non-metalporphyrin and cyaninemerocyanineoxo Nordand a triphenylmethane seriesa xanthene seriesazothe Anthraquinone systemis mentioned as organic coloring matter which carries out mixed use. Methine system coloring mattersuch as a ruthenium complex and merocyanineis mentioned preferably. Although a ratio of coloring matter to mix does not have limitation in particular and it is optimized from each coloring matterit is preferred that beyond a 10% mol grade generally uses it about one coloring matter from mixing of equimolars. It may be the same as that of a case where concentration of the coloring matter sum total in a solution accepts one kind of mixed color matter when adsorbing coloring matter at an oxide semiconductor particle thin film using a mixture solution or a dispersed solutionand it supports.

[0044]When supporting coloring matter to a thin film of an oxide semiconductor particlein order to prevent a meeting of coloring matterit is effective under coexistence of an inclusion compound to support coloring matter. Although steroid system compoundssuch as cholic acidcrown ethercyclodextrina calyx allenepolyethylene oxideetc. are mentioned as an inclusion compound heredesirable things are cholic acidpolyethylene oxideetc. After making coloring matter supportthe semiconductor electrode surface may be processed with amine compoundssuch as 4-t-butylpyridine. A way a method of processing dips a substrate with which a semiconductor particulate film which supported coloring matter was provided in an ethanol solution of amine etc. are taken. A solar cell of this invention comprises a photoelectric conversion element electrodea counter electrodea redox electrolyteor a hole transporting material which made the above-mentioned oxide-semiconductor thin film support coloring matter. Redox electrolytes may be a solution in which a redox couple was dissolved into a solventa gel electrolyte impregnated with a polymer matrixand a solid electrolyte like fused salt. A thing using discotic liquid crystal phasessuch as conductive polymerssuch as an amine derivativepolyacethylenepoly anilineand a polythiopheneand polyphenyleneas a hole transporting material etc. are mentioned. As a counter electrode to be usedit has conductivityand what acts a reduction reaction of a redox electrolyte catalytically is preferred. For exampleplatinumcarbonrhodiuma rutheniumetc. are vapor-deposited to glass or a high polymer filmor what applied a conductive particle can use for it. A halogen oxidation reduction system electrolyte which consists of a halogenated compound and a halogen molecule which use halogen ion as a counter ion as a redox electrolyte used for a solar cell of this inventionAlthough organic acid-ized reduction system electrolytessuch as metal redox system electrolytessuch as metal complexessuch as a ferrocyanic acid salt-ferricyanic acid salt and ferrocene ferricinium ionalkyl thiol alkyl disulfideviologen coloring matterand hydroquinone quinoneetc. can be raisedA halogen oxidation reduction system electrolyte

is preferred. As a halogen molecule in a halogen oxidation reduction system electrolyte which consists of a halogenated compound-halogen moleculemolecular iodinebromine moleculesetc. are raisedfor exampleand molecular iodine is preferred. As a halogenated compound which uses halogen ion as a counter ionFor examplealthough organic quarternary ammonium salt of halogensuch as halogenation metal saltsuch as LiINaIKICsIand CaI$_2$ or tetra alkylammonium iodideimidazolium iodideand pyridinium iodideetc. are raisedA salts compound which uses iodine ion as a counter ion is preferred. As a salts compound which uses iodine ion as a counter ionlithium iodideiodination NARIUMUiodination trimethylammonium saltetc. are raisedfor example.

[0045]When a redox electrolyte comprises a form of a solution containing itan inertness thing is electrochemically used for the solvent. For exampleacetonitrilepropylene carbonateethylene carbonate3-methoxy propionitrilemethoxy acetonitrileethylene glycolPropylene glycola diethylene glycoltriethylene glycolGamma-butyrolactonedimethoxyethanediethyl carbonatediethyletherDiethyl carbonatedimethyl carbonate12-dimethoxyethaneDimethylformamidedimethylsulfoxide13-dioxolaneMethyl formate2-methyltetrahydrofuran3-methoxy OKISAJI lysine 2-oneThey are mentioned by sulfolanea tetrahydrofuranwateretc. and also in theseIn particularacetonitrilepropylene carbonateethylene carbonate3-methoxy propionitrilemethoxy acetonitrileethylene glycoland 3-methoxy OKISAJI lysine 2-one etc. are preferred. These may be independentor may be combined two or more sortsand may be used. In the case of a gel electrolytewhat uses polyacrylatepolymethacrylate resinetc. is mentioned as a matrix. Concentration of a redox electrolyte is usually about 0.1 to 90 % of the weight preferably at 0.01 to 99 % of the weight.

[0046]A solar cell of this invention arranges a counter electrode so that it may be inserted into an electrode of an optoelectric transducer which supported coloring matter to an oxide-semiconductor thin film on a substrate. It is obtained by being filled up with a solution which contained a redox electrolyte between them.

[0047]

[Example]Although this invention is explained still more concretely based on an example belowthis invention is not limited to these examples. Among an exampleunless a part in particular specifies% expresses weight % for a weight section againrespectively.

[0048]1.4 copies of synthetic example 1 quinaldines and 1.9 copies of trimellitic anhydride are dissolved in 20 copies of trichlorobenzenesand 0.1 copy of zinc chloride is added here. After stirring at 190 ** for 24 hoursthe solid which added 40 copies of methanol and deposited was filteredand it swabbed in methanoland driedand 2.8 copies were obtained for the compound 1. Structure was checked by various spectra etc. lambdamax (DMF): 459 nm [0049]2.2 copies of pyromellitic anhydrides and 1.7 copies of 3-hydroxy-2-methylquinoline are added to 30 copies of synthetic example 2 sulfolanesAfter heating at 180 ** and carrying out heating stirring at 200 ** for 1 hourthe solid which added 40 copies of methanol and deposited was filteredand it swabbed in methanoland driedand 3.4 copies of compounds 37 were obtained. Structure was checked by various spectra etc. lambdamax (DMF): 445 nm [0050]1.7 copies of synthetic example 33-hydroxy-2-methylquinoline and 1.9 copies of trimellitic anhydride are dissolved in 20 copies of trichlorobenzenesand 0.1 copy of zinc chloride is added here. After stirring at 190 ** for 24 hoursthe solid which added 40 copies of methanol and deposited was filteredand it swabbed in methanoland driedand 2.8 copies were obtained for the compound 40. Structure was checked by various spectra etc. lambdamax (DMF): 416 nm [0051]The coloring matter expressed with an example general formula (1) was dissolved in EtOH so that it might be set to 3x10 -4M. A porous substrate (semiconductor thin film electrode which sintered porous titanium oxide on the transparent conductive glass electrode) is immersed from 3 hours at a room temperature into this solution overnightmade the coloring matter of general formula (1) structure supportit was made to wash and dry with a solventand the optoelectric transducer of the semiconductor membrane which carried out dye sensitizing was obtained. In Examples 46and 9 and the comparative example 20.2M titanium tetrachloride aqueous solution is dropped at the titanium oxide membrane part of

a semiconductor thin film electrodeand it rinses after 24-hour settlement at a room temperatureThe coloring matter of general formula (1) structure was again supported with 450 degrees in a similar manner using the titanium tetrachloride processing semiconductor thin film electrode obtained by calcinating for 30 minutes. Furthermoreabout Example 3at the time of support of coloring mattercholic acid was added as an inclusion compoundso that it might be set to 3x10 -2Mthe previous coloring matter solution was preparedit supported to semiconductor membraneand cholic-acid-treatment dye sensitizing semiconductor membrane was obtained. The solution which fixes the electrically conductive glass by which weld slag was carried out with platinum in the surface so that it might insert with thisand contains an electrolyte in the opening was poured in. the solution containing an electrolyte -- A and B -- two kinds were prepared. What was dissolved so that the electrolysis solution of A might become 0.1M/0.1M/0.6M/1M at 3-methoxy propionitrilerespectively about an iodine / lithium iodide /1and 2-dimethyl- 3-n-propyl imidazolium iodide / t-butylpyridineIn the solution of 6 to 4 of ethylene carbonate and acetonitrileit dissolved and the electrolysis solution of B prepared iodine / tetra-n-propyl ammonium eye ODAIDO so that it might become 0.02M/0.5M. The size of the cell to measure made the execution effect portion 0.25-cm2. The light source was made into 100 mW/cm2 through AM1.5 filter using 500W xenon lamp. A short-circuit currentrelease voltageand conversion efficiency were measured using POTENSHIO galvanostat.

[0052]

[Formula 16]

[0053]

[Table 5]

[0054]

[Effect of the Invention]In the dye sensitizing optoelectric transducer of this inventionthe solar cell with high conversion efficiency was able to be provided by using the coloring matter of a general formula (1).